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UTILITY PATENT APPLICATION TRANSMITTAL		Attorney Docket No. BA-22580	Total Pages 45
First Named Inventor or Application Identifier			
HIROSHI HASEGAWA, ET AL			
(Only for new nonprovisional applications under 37 CFR 1.53(b))		Express Mail Label No.	EM564188157US

APPLICATION ELEMENTS <i>See MPEP chapter 600 concerning utility patent application contents.</i>		ADDRESS TO: Assistant Commissioner for Patents Box Patent Application Washington, DC 20231	
<p>1. <input checked="" type="checkbox"/> Fee Transmittal Form (Submit an original, and a duplicate for fee processing)</p> <p>2. <input checked="" type="checkbox"/> Specification [Total Pages 37] (preferred arrangement set forth below)</p> <ul style="list-style-type: none"> - Descriptive title of the invention - Cross References to Related Applications - Statement Regarding Fed sponsored R & D - Reference to Microfiche Appendix - Background of the Invention - Brief Summary of the Invention - Brief Description of the Drawings (if filed) - Detailed Description - Claim(s) - Abstract of the Disclosure <p>3. <input type="checkbox"/> Drawing(s) (35 USC 113) [Total Sheets]</p> <p>4. Oath or Declaration [Total Pages 2]</p> <p>a. <input checked="" type="checkbox"/> Newly executed (original or copy)</p> <p>b. <input type="checkbox"/> Copy from a prior application (37 CFR 1.63(d)) (for continuation/divisional with Box 17 completed) [Note Box 5 below]</p> <p>i. <input type="checkbox"/> DELETION OF INVENTOR(S) Signed statement attached deleting inventor(s) named in the prior application, see 37 CFR 1.63(d)(2) and 1.33(b).</p> <p>5. <input type="checkbox"/> Incorporation By Reference (useable if Box 4b is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.</p>		<p>6. <input type="checkbox"/> Microfiche Computer Program (Appendix)</p> <p>7. Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)</p> <p>a. <input type="checkbox"/> Computer Readable Copy</p> <p>b. <input type="checkbox"/> Paper Copy (identical to computer copy)</p> <p>c. <input type="checkbox"/> Statement verifying identity of above copies</p>	
		ACCOMPANYING APPLICATION PARTS	
		<p>8. <input checked="" type="checkbox"/> Assignment Papers (cover sheet & document(s))</p> <p>9. <input type="checkbox"/> 37 CFR 3.73(b) Statement (when there is an assignee) <input type="checkbox"/> Power of Attorney</p> <p>10. <input type="checkbox"/> English Translation Document (if applicable)</p> <p>11. <input type="checkbox"/> Information Disclosure Statement (IDS)/PTO-1449 <input type="checkbox"/> Copies of IDS Citations</p> <p>12. <input type="checkbox"/> Preliminary Amendment</p> <p>13. <input checked="" type="checkbox"/> Return Receipt Postcard (MPEP 503) (Should be specifically itemized)</p> <p>14. <input type="checkbox"/> Small Entity <input type="checkbox"/> Statement filed in prior application, Statement(s) <input type="checkbox"/> Status still proper and desired</p> <p>15. <input type="checkbox"/> Certified Copy of Priority Document(s) (if foreign priority is claimed)</p> <p>16. <input type="checkbox"/> Other:</p>	

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FEE TRANSMITTAL	Complete if Known	
	Application Number	
	Filing Date	
	First Named Inventor	HIROSHI HASEGAWA
	Group Art Unit	
	Examiner Name	
	Attorney Docket Number	BA-22580
TOTAL AMOUNT OF PAYMENT (\$1,982.00)		

METHOD OF PAYMENT (check one)		FEE CALCULATION (continued)																																																																																																																									
1. <input type="checkbox"/> The Commissioner is hereby authorized to charge indicated fees and credit any over payments to: Deposit Account Number _____ Deposit Account Number _____ <input type="checkbox"/> Charge Any Additional Fee Required Under 37 CFR 1.18 and 1.17 <input type="checkbox"/> Charge the Issue Fee Set in 37 CFR 1.18 at the Making of the Notice of Allowance		3. ADDITIONAL FEES <table border="1"> <thead> <tr> <th>Large Entity Fee Code (\$)</th> <th>Small Entity Fee Code (\$)</th> <th>Fee Description</th> <th>Fee Paid</th> </tr> </thead> <tbody> <tr> <td>105 130 205 65</td> <td></td> <td>Surcharge - late filing fee or oath</td> <td></td> </tr> <tr> <td>127 50 227 25</td> <td></td> <td>Surcharge - late provisional filing fee or cover sheet</td> <td></td> </tr> <tr> <td>139 130 139 130</td> <td></td> <td>Non-English specification</td> <td></td> </tr> <tr> <td>147 2,520 147 2,520</td> <td></td> <td>For filing a request for reexamination</td> <td></td> </tr> <tr> <td>112 920* 112 920*</td> <td></td> <td>Requesting publication of SIR prior to Examiner action</td> <td></td> </tr> <tr> <td>113 1,840* 113 1,840*</td> <td></td> <td>Requesting publication of SIR after Examiner action</td> <td></td> </tr> <tr> <td>115 110 215 55</td> <td></td> <td>Extension for reply within first month</td> <td></td> </tr> <tr> <td>116 400 216 200</td> <td></td> <td>Extension for reply within second month</td> <td></td> </tr> <tr> <td>117 950 217 475</td> <td></td> <td>Extension for reply within third month</td> <td></td> </tr> <tr> <td>118 1,510 218 755</td> <td></td> <td>Extension for reply within fourth month</td> <td></td> </tr> <tr> <td>128 2,060 228 1,030</td> <td></td> <td>Extension for reply within fifth month</td> <td></td> </tr> <tr> <td>119 310 219 155</td> <td></td> <td>Notice of Appeal</td> <td></td> </tr> <tr> <td>120 310 220 155</td> <td></td> <td>Filing a brief in support of an appeal</td> <td></td> </tr> <tr> <td>121 270 221 135</td> <td></td> <td>Request for oral hearing</td> <td></td> </tr> <tr> <td>138 1,510 138 1,510</td> <td></td> <td>Petition to institute a public use proceeding</td> <td></td> </tr> <tr> <td>140 110 240 55</td> <td></td> <td>Petition to revive - unavoidable</td> <td></td> </tr> <tr> <td>141 1,320 241 660</td> <td></td> <td>Petition to revive - unintentional</td> <td></td> </tr> <tr> <td>142 1,320 242 660</td> <td></td> <td>Utility issue fee (or reissue)</td> <td></td> </tr> <tr> <td>143 460 243 225</td> <td></td> <td>Design issue fee</td> <td></td> </tr> <tr> <td>144 670 244 335</td> <td></td> <td>Plant issue fee</td> <td></td> </tr> <tr> <td>122 130 122 130</td> <td></td> <td>Petitions to the Commissioner</td> <td></td> </tr> <tr> <td>123 50 123 50</td> <td></td> <td>Petitions related to provisional applications</td> <td></td> </tr> <tr> <td>125 240 125 240</td> <td></td> <td>Submission of Information Disclosure Sheet</td> <td></td> </tr> <tr> <td>581 40 581 40</td> <td></td> <td>Recording each patent assignment per property (times number of properties)</td> <td></td> </tr> <tr> <td>146 790 246 395</td> <td></td> <td>Filing a submission after final rejection (37 CFR 1.129(a))</td> <td></td> </tr> <tr> <td>149 790 249 395</td> <td></td> <td>For each additional invention to be examined (37 CFR 1.129(b))</td> <td></td> </tr> <tr> <td colspan="2">Other fee (specify) _____</td> <td colspan="2"></td> </tr> <tr> <td colspan="2">Other fee (specify) _____</td> <td colspan="2"></td> </tr> <tr> <td colspan="2"> * Reduced by Basic Filing Fee Paid </td> <td colspan="2"> SUBTOTAL (3) (\$) </td> </tr> </tbody></table>		Large Entity Fee Code (\$)	Small Entity Fee Code (\$)	Fee Description	Fee Paid	105 130 205 65		Surcharge - late filing fee or oath		127 50 227 25		Surcharge - late provisional filing fee or cover sheet		139 130 139 130		Non-English specification		147 2,520 147 2,520		For filing a request for reexamination		112 920* 112 920*		Requesting publication of SIR prior to Examiner action		113 1,840* 113 1,840*		Requesting publication of SIR after Examiner action		115 110 215 55		Extension for reply within first month		116 400 216 200		Extension for reply within second month		117 950 217 475		Extension for reply within third month		118 1,510 218 755		Extension for reply within fourth month		128 2,060 228 1,030		Extension for reply within fifth month		119 310 219 155		Notice of Appeal		120 310 220 155		Filing a brief in support of an appeal		121 270 221 135		Request for oral hearing		138 1,510 138 1,510		Petition to institute a public use proceeding		140 110 240 55		Petition to revive - unavoidable		141 1,320 241 660		Petition to revive - unintentional		142 1,320 242 660		Utility issue fee (or reissue)		143 460 243 225		Design issue fee		144 670 244 335		Plant issue fee		122 130 122 130		Petitions to the Commissioner		123 50 123 50		Petitions related to provisional applications		125 240 125 240		Submission of Information Disclosure Sheet		581 40 581 40		Recording each patent assignment per property (times number of properties)		146 790 246 395		Filing a submission after final rejection (37 CFR 1.129(a))		149 790 249 395		For each additional invention to be examined (37 CFR 1.129(b))		Other fee (specify) _____				Other fee (specify) _____				* Reduced by Basic Filing Fee Paid		SUBTOTAL (3) (\$)	
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SUBMITTED BY		Complete (if applicable)	
Typed or Printed Name	FERNANDA M. FIORDALISI	Reg. Number	20,938
Signature	<i>Fernanda M. Fiordalisi</i>	Date	4/9/98
		Deposit Account	User ID

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FLUID COMPOSITIONS CONTAINING REFRIGERATOR
OILS AND CHLORINE-FREE FLUOROCARBON REFRIGERANTS

5

Background of the Invention

1. Field of the Invention

10 This invention relates to a fluid composition for
compressors of refrigerators comprising a chlorine-free
fluorocarbon as a refrigerant and a lubricating oil (the oil
being hereinafter referred to as "a refrigerator oil for use
with a chlorine-free fluorocarbon refrigerant") and, more
specifically, it relates to such a fluid composition which
15 comprises a specific ester as a base oil and is superior in
various properties.

2. Prior Art

Generally, naphthenic mineral oils, paraffinic
mineral oils, alkylbenzenes, polyglycolic oils, ester oils
20 and mixtures thereof, which have each a kinematic viscosity
of 10 - 200 cSt at 40°C, as well as these oils incorporated
with suitable additives have been used as refrigerator oils.

On the other hand, chlorofluorocarbons (CFCS) type
refrigerants, such as CFC-11, CFC-12, CFC-113 and HCFC-22,
25 have been used for refrigerators.

Of these CFCS, CFCS such as CFC-11, CFC-12 and CFC-
113, which are obtained by substituting all the hydrogen

atoms of hydrocarbons thereof by halogen atoms including chlorine atoms, may lead to the destruction of the ozone layer, and therefore, the use of the CFCS has been controlled. Accordingly, chlorine-free fluorocarbons, such as HFC-134a and HFC-152a, have been being used as substitutes for CFCS. HFC-134a is especially promising as a substitute refrigerant since it is similar in thermodynamic properties to CFC-12 which has heretofore been used in many kinds of refrigerators of home cold-storage chests, air-conditioners and the like.

Refrigerator oils require various properties, among which their compatibility with refrigerants is extremely important in regard to lubricity and system efficiency in refrigerators. However, conventional refrigerator oils comprising, as the base oils, naphthenic oils, paraffinic oils, alkylbenzenes, heretofore known ester oils and the like, are hardly compatible with chlorine-free fluorocarbons such as HFC-134a. Therefore, if said conventional refrigerator oils are used in combination with HFC-134a, the resulting mixture will separate into two layers at normal temperature so as to degrade the oil-returnability which is the most important within the refrigeration system and cause various troubles such as a decrease in refrigeration efficiency, the deterioration of lubricity and the consequent seizure of the compressor within the system whereby the refrigerator oils are made unsuitable for use as such. In addition, polyglycolic oils are also known as

refrigerator oils for their high viscosity index and are disclosed in, for example, JP-A-57-42119 and JP-A-61-52880 and JP-A-57-51795. However, the polyglycolic oils disclosed in these prior art publications are not fully compatible with HFC-134a thereby raising the same problems as above and rendering them unusable.

Further, US-A-4,755,316 discloses polyglycolic refrigerator oils which are compatible with HFC-134a and US-A-4,851,144 discloses refrigerator oils comprising a mixture of an ester and a polyglycol which are compatible with HFC-134a. In addition, the present inventors developed polyglycolic refrigerator oils which have excellent compatibility with HFC-134a as compared with conventional known refrigerator oils, filed an application for a patent for the thus developed polyglycolic refrigerator oils and have already obtained a patent (US-A-4,948,525) therefor. It has been found, however, that the polyglycolic oils raise problems as to their high compatibility with water and inferior electrical insulating property.

On the other hand, refrigerator oils used in compressors of home refrigerators and the like are required to have a high electrical insulating property. Among the known refrigerator oils, alkylbenzenes and the mineral oils have the highest insulating property, but they are hardly compatible with chlorine-free fluorocarbons such as HFC-134a as mentioned above. WO 90/12849 describes a composition comprising a hydrogen-containing halogenocarbon and a

specific ester lubricant. No refrigerator oil having both high compatibility with chlorine-free fluorocarbons such as HFC-134a and a high insulating property has been developed prior to the present invention.

5

Summary of the Invention

10 The present inventors made various intensive studies in attempts to develop refrigerator oils which can meet the aforesaid requirements and, as the result of their studies, they found that esters having specific structures have excellent compatibility with chlorine-free fluorocarbons such as HFC-134a, a high electrical insulating property, and a low pour point as well as excellent lubricity. The
15 present invention is based on this finding.

The object of the present invention is to provide fluid compositions comprising a refrigerator oil and a chlorine-free fluorocarbon refrigerant, the oil comprising as a major component (or a base oil) an tetraester having a
20 specific structure and having excellent compatibility with chlorine-free fluorocarbons such as HFC-134a, high electrical insulating property, high wear resistance, low hygroscopicity, and high thermal and chemical stability.

25 The present invention provides a fluid composition for a refrigerator, which comprises a chlorine-free fluorocarbon refrigerant and a refrigerator oil, said

refrigerator oil consisting essentially of a tetraester of pentaerythritol of formula (1)



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with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

10 The tetraester products obtained by any conventional methods may be refined to remove the by-products and/or unreacted reactants, but the by-products and/or unreacted reactants may be present in small amounts in the refrigerator oils according to the present invention as far as they do not impair the excellent performances thereof.

15 In the preparation of the refrigerator oil according to the present invention, the ester mentioned above may be used singly, or jointly as a mixture of at least one kind of other esters for adding to the base oil.

20 The kinematic viscosities of the base oil according to the present invention are in the range of preferably 2-150 cSt, more preferably 5-100 cSt at 100°C.

25 The refrigerator oil according to the present invention may contain as the only base oil the tetraester of pentaerithritol with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid and, as required, it may be incorporated with paraffinic mineral oils, naphthenic mineral oils, poly α -olefins, alkylbenzenes and the like.

but, in this case, the resulting mixed oil will be lowered in compatibility with hydrogen-containing halogonocarbons.

The amount of these conventional oils so incorporated is not particularly limited as far as the excellent
5 performances of the refrigerator oil according to the present invention are not impaired, but the tetraester of pentaerythritol with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid should be present in the resulting mixed oil in a ratio of usually more than 50 % by weight,
10 preferably not less than 70 % by weight of the total amount of the mixed oil.

To further improve the refrigerator oil according to the present invention in thermal stability and chemical stability, it is incorporated with at least one kind of an
15 epoxy compound. The epoxy compound used herein is preferably selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, aryloxirane compounds, alkyloxirane compounds, alicyclic
20 epoxy compounds, epoxidized fatty acid monoesters and epoxidized vegetable oils.

The said phenylglycidyl ether epoxy compounds used herein include phenylglycidyl ether and derivatives thereof such as alkylphenylglycidyl ethers. The said
25 alkylphenylglycidyl ethers are those having 1 to 3 alkyl groups having 1 to 13 carbon atoms, among which are preferred those having an alkyl group having 4 to 10 carbon

atoms, such as n-butylphenylglycidyl ether, i-butylphenylglycidyl ether, sec-butylphenylglycidyl ether, tert-butylphenylglycidyl ether, pentylphenylglycidyl ether, hexylphenylglycidyl ether, heptylphenylglycidyl ether, 5 octylphenylglycidyl ether, nonylphenylglycidyl ether and decylphenylglycidyl ether.

The alkylglycidyl ether epoxy compounds include decylglycidyl ether, undecylglycidyl ether, dodecylglycidyl ether, tridecylglycidyl ether, tetradecylglycidyl ether, 2-ethylhexylglycidyl ether, neopentyl glycol diglycidyl ether, 10 trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, 1,6-hexanediol diglycidyl ether, sorbitol polyglycidyl ether, polyalkylene glycol monoglycidyl ethers and polyalkylene glycol diglycidyl 15 ethers.

The glycidyl ester epoxy compounds include phenylglycidyl esters, alkylglycidyl esters and alkenylglycidyl esters with glycidyl 2,2-dimethyl octanoate, glycidyl benzoate, glycidyl acrylate, glycidyl methacrylate 20 and the like being preferred.

The aryloxirane compounds include 1,2-epoxystyrene and alkyl-1,2-epoxystyrene.

The alkyloxirane compounds include 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, 1,2-epoxyheptane, 1,2-epoxyoctane, 1,2-epoxynonane, 1,2-epoxydecane, 1,2-epoxyundecane, 1,2-epoxydodecane, 1,2-epoxytridecane, 1,2-epoxytetradecane, 1,2-epoxypentadecane, 1,2-epoxyhexadecane, 25

1,2-epoxyheptadecane, 1,1,2-epoxyoctadecane, 2-epoxynonadecane and 1,2-epoxyeicosane.

The alicyclic epoxy compounds include 1,2-epoxycyclohexane, 1,2-epoxycyclopentane, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, bis (3,4-epoxycyclohexylmethyl) adipate, exo-2,3-epoxynorbornane, bis (3,4-epoxy-6-methylcyclohexylmethyl) adipate, 2-(7-oxabicyclo[4.1.0]hept-3-yl)-spiro(1,3-dioxane-5,3'-[7]oxabicyclo[4.1.0]heptane, 4-(1'-methylepoxyethyl)-1,2-epoxy-2-methylcyclohexane and 4-epoxyethyl-1,2-epoxycyclohexane.

The epoxidized fatty acid monoesters include esters of an epoxidized fatty acid having 12 to 20 carbon atoms and an alcohol having 1 to 8 carbon atoms, phenol or an alkylphenol. In particular, butyl, hexyl, benzyl, cyclohexyl, methoxyethyl, octyl, phenyl or butylphenyl esters of epoxidized stearic acid may preferably be used.

The epoxidized vegetable oils include epoxidized compounds of vegetable oils such as soybean oil, linseed oil and cottonseed oil.

Among these epoxy compounds, the preferable ones include phenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds and alicyclic epoxy compounds.

It is desirable that these epoxy compounds be incorporated in the refrigerator oil according to the present invention in a ratio of 0.1-5.0% by weight,

preferably 0.2-2.0% by weight, of the total amount of the refrigerator oil.

The refrigerator oil composition according to the present invention may be incorporated further with at least one kind of a phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters and phosphorous esters, to improve the oil composition in wear resistance and load resistance. These phosphorus compounds are esters of phosphoric acid or phosphorous acid and an alkanol or a polyether type alcohol, or derivatives of the esters. The phosphoric esters are exemplified by tributyl phosphate, triphenyl phosphate and tricresyl phosphate. The acid phosphoric esters are exemplified by ditetradecyl acid phosphate, dipentadecyl acid phosphate, dihexadecyl acid phosphate, diheptadecyl acid phosphate and dioctadecyl acid phosphate. The amine salts of acid phosphoric esters are exemplified by salts of the above acid phosphoric esters and amines such as methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dipentylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tripropylamine, tributylamine, tripentylamine, trihexylamine, triheptylamine and trioctylamine. The chlorinated phosphoric esters are exemplified by tris-dichloropropyl phosphate.

tris-chloroethyl phosphate,
polyoxyalkylene-bis[di(chloroalkyl)] phosphate and
tris-chlorophenyl phosphate. The phosphorous esters are
exemplified by dibutyl phosphite, tributyl phosphite,

- 5 dipentyl phosphite, tripentyl phosphite, dihexyl phosphite,
trihexyl phosphite, diheptyl phosphite, triheptyl phosphite,
dioctyl phosphite, trioctyl phosphite, dinonyl phosphite,
didecyl phosphite, diundecyl phosphite, triundecyl
phosphite, didodecyl phosphite, tridodecyl phosphite,
10 diphenyl phosphite, triphenyl phosphite, dicresyl phosphite,
tricresyl phosphite and mixtures thereof. These phosphorus
compounds may be added to the refrigerator oil in a ratio of
0.1-5.0 % by weight, preferably 0.2-2.0 % by weight, of the
total amount of the refrigerator oil.

- 15 Of course, both of the aforementioned phosphorus
compounds and epoxy compounds may be used jointly.

- To further enhance the refrigerator oil according to
the present invention in performances, the refrigerator oil
may be incorporated, as required, with heretofore known
20 additives for a refrigerator oil, which include phenol-type
antioxidants such as di-tert.-butyl-p-cresol and bisphenol
A; amine-type antioxidants such as phenyl- α -naphthylamine
and N,N-di(2-naphthyl)-p-phenylenediamine; wear resistant
additives such as zinc dithiophosphate; extreme pressure
25 agents such as chlorinated paraffin and sulfur compounds;
oiliness improvers such as fatty acids; antifoaming agents
such as silicone-type ones; and metal inactivators such as

benzotriazole. These additives may be used singly or jointly. The total amount of these additives added is ordinarily not more than 10 % by weight, preferably not more than 5 % by weight, of the total amount of the refrigerator oil.

The refrigerator oils according to the present invention consisting essentially of a tetraester of pentacrythritol with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid as the base oil should have such viscosity and pour point as those which are normally suitable for an ordinary refrigerator oil, but they should have a pour point of not higher than -10°C , preferably -20°C to -80°C , to prevent them from solidification at a low temperature. Further, they should desirably have a kinematic viscosity of not less than 2cSt, preferably not less than 3cSt at 100°C , to keep the sealability of the compressor when used, while they should desirably have a kinematic viscosity of not more than 150cSt, preferably not more than 100cSt at 100°C , in view of their fluidity at a low temperature and the efficiency of heat exchange in the evaporator when used.

The refrigerants which may be used in refrigerators in which the fluid composition of the present invention are suitably used, include chlorine-free fluorocarbons such as alkane fluorides having 1-3 carbon atoms, preferably 1-2 carbon atoms. The said chlorine-free fluorocarbons are exemplified by HFCs (chlorine-free type halogenocarbons)

such as difluoromethane (HFC-32), trifluoromethane (HFC-23), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoroethane (HFC-152a) and mixtures thereof. Among these chlorine-free fluorocarbons, HFC-32, HFC-23, HFC-125, HFC-134, HFC-134a and HFC-152a, are preferable in view of the environmental problems. The refrigerant used may suitably be selected from these halogenocarbons mentioned above depending on the purpose for which the resulting refrigerant is used as well as the properties which are desirable for the resulting refrigerant. The preferable refrigerants are exemplified by HFC-134a; a mixture of HFC-134a (60-80wt%) and HFC-32 (40-20wt%); a mixture of HFC-32 (50-70wt%) and HFC-125 (50-30wt%); a mixture of HFC-134a (60wt%), HFC-32 (30wt%) and HFC-125 (10wt%); a mixture of HFC-134a (52wt%), HFC-32 (23wt%) and HFC-125 (25wt%); and a mixture of HFC-143a (52wt%), HFC-125 (44wt%) and HFC-134a (4wt%).

The fluid composition of the present invention for use in a refrigerator is a mixture of the refrigerator oil and a chlorine-free halogenocarbon such as an alkane fluoride as mentioned above.

The mixing ratio of the refrigerator oil and the refrigerant in the resulting composition is not particularly limited, but the refrigerator oil is usually comprised in an amount of 1-500 parts by weight, preferably in an amount of

2-400 parts by weight, based on 100 parts by weight of the refrigerant.

The refrigerator oils according to the present invention are very excellent in compatibility with the hydrogen-containing halogenocarbons as compared with the heretofore known refrigerator oils. Further, the refrigerator oils according to the present invention are excellent because they have not only high compatibility with the hydrogen-containing halogenocarbons and high electrical insulating property but also high lubricity, low hygroscopicity, low pour point and high thermal and chemical stability.

The fluid compositions of the present invention may particularly preferably be used in refrigerators, air-conditioners, dehumidifiers, cold-storage chests, freezers, freeze and refrigeration warehouses, automatic vending machines, showcases, cooling units in chemical plants, and the like which have a reciprocating or rotary compressor. Further, the above refrigerator oils may also preferably be used in refrigerators having a centrifugal compressor.

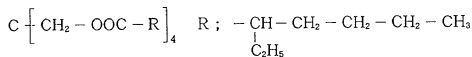
The present invention will be better understood by the following Examples and Comparative Examples.

Examples 1-2 and Comparative Examples 1-14

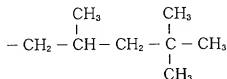
First, base oils according to the present invention (Base oil 1) and comparative base oils (Base oils 2-13),

which are used in the Examples and Comparative Examples, respectively, are illustrated as follows:

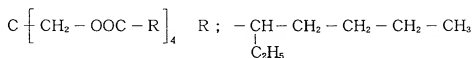
[Base oil 1] A tetraester of pentaerythritol (1 mol), 2-ethylhexanoic acid (2 mol) and 3,5,5-trimethylhexanoic acid (2 mol)



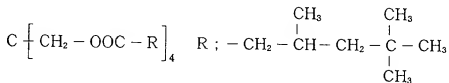
or



[Base oil 2] A tetraester of pentaerythritol (1 mol) and 2-ethylhexanoic acid (4 mol):



[Base oil 3] A tetraester of pentaerythritol (1 mol) and 3,5,5-trimethylhexanoic acid (4 mol):



[Base oil 4] A naphthenic mineral oil

[Base oil 5] A branched-chain type alkylbenzene (average molecular weight: about 300)

[Base oil 6] Polyoxypropylene glycol monobutyl ether (average molecular weight: about 500)

[Base oil 7] Polyoxypropylene glycol monobutyl ether
(average molecular weight: about 1000)

5 [Base oil 8] Polyoxypropylene glycol (average molecular
weight: about 700)

[Base oil 9] Polyoxypropylene glycol (average molecular
weight: about 2000)

10 [Base oil 10] A tetraester of pentaerythritol (1 mol) and
n-nonanoic acid (4 mol):

[Base oil 11] A tetraester of pentaerythritol (1 mol) and
coconut oil

15 [Base oil 12] A triester of trimethylolpropane (1 mol) and
n-nonanoic acid (3 mol):

20 [Base oil 13] A triester of trimethylolpropane (1 mol) and
coconut oil

The refrigerator oils of Examples 1-2 according to
the present invention each of which has a composition
indicated in the following Table 1 were prepared and then
25 evaluated for their performances that are their miscibility
with HFC-134a, insulating property, wear resistance,
hygroscopicity and thermal and chemical stability by the

following respective test methods. The results thus obtained are indicated in Table 1.

For comparison, the ester of pentaerithritol with 2-ethylhexanoic acid (Comparative Examples 1 and 2), the ester of pentaerithritol with 3,5,5-trimethylhexanoic acid (Comparative Examples 3 and 4), the mineral oil (Comparative Example 5), the alkylbenzene (Comparative Example 6), the polypropylene glycol monoalkyl ethers (Comparative Examples 7 and 8), the polypropylene glycols (Comparative Examples 9 and 10) and the straight-chain fatty acid esters of polyol alcohols (Comparative Examples 11-14) which have heretofore been used as refrigerator oils were evaluated for their performances in the same manner as in Examples 1-2. The results thus obtained are also indicated in Table 1.

(Miscibility with HFC-134a)

0.2 g of the test oil of each of the Examples and the Comparative Examples and 1.8 g of the refrigerant (HFC-134a) were sealed in a glass tube having an inner diameter of 6 mm and a length of 220 mm. This glass tube was then placed in a thermostat maintained at a predetermined low temperature or high temperature to observe whether the refrigerant and the test oil were miscible with each other, separated from each other or made white-turbid.

(Insulating property)

The test oils were each measured for specific volume resistivity at 25°C in accordance with JIS C 2101.

(FALEX wear test)

5 The test oils were each applied to a test journal for measuring the amount of the test journal worn by having the journal run in at a test oil temperature of 100 °C under a load of 150 lb for 1 minute and then running it under a load of 250 lb for 2 hours in accordance with ASTM D 2670.

10

(Hygroscopicity)

 Thirty grams (30 g) of each of the test oils were placed in a 300-ml beaker, allowed to stand for 7 days in an air-conditioned bath maintained at a temperature of 60 °C and a humidity of 30 % and then measured for water content by the Karl-Fischer method.

15

(Thermal and chemical stability)

 Thermal and chemical stabilities of the test oils were evaluated by the following sealed tube test with HFC-134a in accordance with JIS K 2211 4.9.

20

 An equi-volume mixture of each of the test oils and the refrigerant (HFC-134a) was sealed, together with copper, iron and aluminum catalysts, in a glass tube and then heated to 250°C for 168 hours to observe discoloration of the test oil and surface states of the catalysts and determine the degree of discoloration. The degree of discoloration of the

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test oil was classified into 9 grades ranging from 0 (no discoloration) to 8 (black-brown color).

(Pour point)

5 The test oils are each measured for specific pour point in accordance with JIS K 2269.

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T a b l e 1

Examples Comparative Examples	Base oils	Epoxy compounds*		Kinematic viscosity @ 100°C (mm ² /s)	Miscibility with HFC-134a Miscible Temperature Range (°C)	Resistivity @25°C (Ωcm)	Patex test Amount of journal worn (mg)	Ilygro- scopicity 60°C, 30% (%)	Sealed tube test				Pour point (°C)	
		Kind	Amount (Out wt %)						Oil color	Catalysts				
										Cu	Fe	Al		
Example 1	1	None	-	8.1	-28~37**	4.0×10 ¹⁴	26	0.19	5	No change	Luster decreased	No change	-45	
Example 2	1	t-BuPGE	0.5	8.1	-28~37**	3.9×10 ¹⁴	26	0.18	1	No change	No change	No change	No change	-45
Com. Ex. 1	2	None	-	6.2	-27~37**	4.1×10 ¹⁴	27	0.19	4	No change	Luster decreased	No change	No change	0
Com. Ex. 2	2	PdE	0.5	6.2	-27~37**	4.2×10 ¹⁴	26	0.19	1	No change	No change	No change	No change	0
Com. Ex. 3	3	None	-	11.5	-32~37**	3.8×10 ¹⁴	25	0.19	4	No change	Luster decreased	No change	No change	10
Com. Ex. 4	3	s-BuPGE	0.5	11.5	-32~37**	3.8×10 ¹⁴	25	0.20	1	No change	No change	No change	No change	10
Com. Ex. 5	4	None	-	5.1	Immiscible	3.8×10 ¹⁴	23	0.01	-	-	-	-	-	-
Com. Ex. 6	5	None	-	4.8	Immiscible	6.4×10 ¹⁴	25	0.01	-	-	-	-	-	-
Com. Ex. 7	6	None	-	4.9	<70~97	1.1×10 ¹¹	40	1.31	-	-	-	-	-	-
Com. Ex. 8	7	None	-	10.8	<70~56	1.2×10 ¹¹	35	1.01	-	-	-	-	-	-
Com. Ex. 9	8	None	-	10.6	<70~64	5.6×10 ¹⁰	38	2.30	-	-	-	-	-	-
Com. Ex. 10	9	None	-	22.4	-51~32	4.8×10 ¹⁰	30	1.81	-	-	-	-	-	-
Com. Ex. 11	10	None	-	6.1	Immiscible	-	-	-	-	-	-	-	-	-
Com. Ex. 12	11	None	-	4.9	Immiscible	-	-	-	-	-	-	-	-	-
Com. Ex. 13	12	None	-	5.4	Immiscible	-	-	-	-	-	-	-	-	-
Com. Ex. 14	13	None	-	4.4	Immiscible	-	-	-	-	-	-	-	-	-

* POE : Phenyl Glycidyl Ether

s-BuPGE : s-Butylphenyl Glycidyl Ether

t-BuPGE : t-Butylphenyl Glycidyl Ether

** CT: Critical temperature of HFC-134a (102°C)

It is apparent from the results indicated in Table 1 that the refrigerator oils (Examples 1 and 2) according to the present invention are excellent in miscibility with a refrigerant, HFC-134a, as compared with those of Comparative Examples 5-6 and 11-14.

As is apparent from the results indicated in Table 1, the esters of Comparative Examples 11 and 13 in which the alkyl groups of the acid moiety are all straight-chain ones are inferior in miscibility with the refrigerant. Further, Table 1 shows that the esters of Comparative Examples 12 and 14 which have heretofore been used as lubricating oils, refrigerator oils and the like and in which the acid moiety is originated from a natural fat or oil, are also inferior in miscibility with the refrigerant.

Table 1 further shows that the ethers of Comparative Examples 7 and 8 as well as the polyoxypropylene glycols of Comparative Examples 9 and 10 are excellent in miscibility with the refrigerant, but these ethers and glycols are inferior in insulating property thereby rendering them unusable for hermetic type compressors. Still further, Table 1 shows that the ethers and glycols of Comparative Examples 7-10 have hygroscopicity 5-10 times that of the refrigerator oils of Examples 1 and 2 and are also inferior in electrical insulating property, ice choke, wear resistance, stability and the like to the refrigerator oils of the Examples.

The FALEX wear test shows that the refrigerator oils of Examples 1 and 2 are at least equal in wear resistance to those of Comparative Examples 7-10.

5 The esters of Comparative Examples 1-4 are at least equivalent to those of Examples 1 and 2 in miscibility with HFC-134a, insulating property, wear resistance and hygroscopicity, but, as is apparent from the results indicated in Table 1 that the refrigerator oils (Examples 1 and 2) according to the present invention is excellent in
10 thermal stability having low pour point as compared with those of Comparative Examples 1-4.

The results of the sealed tube test shows that the refrigerator oils of Example 2 is still more excellent in thermal and chemical stability as compared with the
15 refrigerator oil of Example 1 as well as the refrigerator oils of Comparative Examples 1 and 3.

(Effect of the Invention)

As is apparent from the above comparative
20 experiments, the refrigerator oils according to the present invention are suitable for use in refrigerators using therein a hydrogen-containing halogenocarbon as a refrigerant and are excellent in electrical insulating property, wear resistance, nonhygroscopicity and thermal and
25 chemical stability. In other words, the refrigerator oils according to the present invention excellently have all properties which are important for refrigerator oils.

What is claimed is:

1. A fluid composition for a refrigerator, which comprises a chlorine-free fluorocarbon refrigerant and a refrigerator oil, said refrigerator oil consisting essentially of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid, said refrigerator oil exhibiting a pour point not higher than -10°C .

2. The fluid composition according to claim 1 wherein said refrigerator oil has a pour point of -20°C to -80°C .

3. The fluid composition according to claim 1 wherein said 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid are in a molar ratio of 1:1.

4. The fluid composition according to claim 1 which additionally contains 0.1-5% by weight based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds,

alicyclic epoxy compounds and epoxidized fatty acid monoesters.

5 5. The fluid composition according to claim 1 which additionally contains at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters.

10 6. The fluid composition according to claim 1 which additionally contains at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antiforming agents and metal inactivators.

15 7. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil being a tetraester of pentaerythritol of formula (1)

20



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with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid, said refrigerator oil exhibiting a pour point not higher than -10°C .

8. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil
5 consisting of a tetraester of pentaerythritol of formula (1)



10 with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and 0.1-5% by weight based on the total amount of said refrigerator oil of at least one epoxy compound selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds,
15 alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters and said refrigerator oil exhibiting a pour point not higher than -10°C .

20 9. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of
25 pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes and said refrigerator oil exhibiting a pour point not higher than -10°C.

10. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerator of a refrigerator oil, said refrigerator oil consisting of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and 0.1-5.0 % by weight based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters and said refrigerator oil exhibiting a pour point not higher than -10°C.

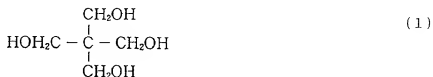
11. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said

refrigerant of a refrigerator oil, said refrigerator oil consisting of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

12. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; and 0.1-5% by weight

based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters and said refrigerator oil exhibiting a pour point not higher than -10°C .

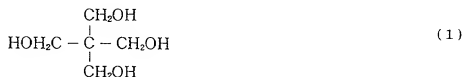
13. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil being a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; 0.1-5% by weight based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; and 0.1-5.0 % by weight

based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters and said refrigerator oil exhibiting a pour point not higher than -10°C.

14. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil being a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; 0.1-5.0 % by weight based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming

agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

15. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; and 0.1-5.0 % by weight based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters and said refrigerator oil exhibiting a pour point not higher than -10°C .

16. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said

refrigerant of a refrigerator oil, said refrigerator oil being a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; 0.1-5% by weight based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C.

17. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

18. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; 0.1-5% by weight

based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; and 0.1-5.0 % by weight based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters and said refrigerator oil exhibiting a pour point not higher than -10°C .

19. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; 0.1-5.0 % by weight

based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

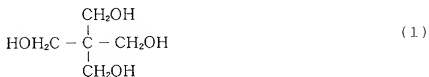
20. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; 0.1-5% by weight based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds,

alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; 0.1-5.0 % by weight based on the total amount of said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C.

21. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, polyα-olefins and alkylbenzenes; 0.1-5% by weight

based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; and not more than 10% by weight of at least one additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

22. A fluid composition for a refrigerator, which consists of a chlorine-free fluorocarbon refrigerant and 1-500 parts by weight based on 100 parts by weight of said refrigerant of a refrigerator oil, said refrigerator oil consisting of as a major component a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid; at least one conventional oil selected from the group consisting of paraffinic mineral oils, naphthenic mineral oils, poly α -olefins and alkylbenzenes; 0.1-5 % by weight

based on the total amount of said refrigerator oil of at least one epoxy compound, said epoxy compound being a member selected from the group consisting of phenylglycidyl ether epoxy compounds, alkylphenylglycidyl ether epoxy compounds, alkylglycidyl ether epoxy compounds, glycidyl ester epoxy compounds, allyloxirane compounds, alkyloxirane compounds, alicyclic epoxy compounds and epoxidized fatty acid monoesters; 0.1-5.0 % by weight based on the total amount of

said refrigerator oil of at least one phosphorus compound selected from the group consisting of phosphoric esters, acid phosphoric esters, amine salts of acid phosphoric esters, chlorinated phosphoric esters, and phosphorous esters; and not more than 10% by weight of at least one

additive selected from the group consisting of phenol antioxidants, amine antioxidants, wear resistant additives, extreme pressure agents, oiliness improvers, antifoaming agents and metal inactivators and said refrigerator oil exhibiting a pour point not higher than -10°C .

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ABSTRACT OF THE DISCLOSURE

A fluid composition for a refrigerator, which comprises a chlorine-free fluorocarbon refrigerant and a refrigerator oil, said refrigerator oil consisting essentially of a tetraester of pentaerythritol of formula (1)



with both 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid, said refrigerator oil exhibiting a pour point not higher than -10°C .

Declaration, Power of Attorney, and Petition

As a below named inventor, I hereby declare that:

Page 1 of 2

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled FLUID COMPOSITIONS CONTAINING REFRIGERATOR OILS AND CHLORINE-FREE, FLUOROCARBON REFRIGERANTS

(check one) ☒ is attached hereto. ☐ was filed on _____ the specification of which Application Serial No. _____ as _____ and was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Hei. (Number)	Japan (Country)	December 28, 1989 (Day/month/year filed)	Priority claimed Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>
1-341244	Japan	December 28, 1989	Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>
1-341245	Japan	December 28, 1989	Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>
2-105772	Japan	April 20, 1990	Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>
2-121133	Japan	May 15, 1990	Yes <input checked="" type="checkbox"/> No <input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.) (Filing date) (Status) (published, pending, abandoned)

(Application Serial No.) (Filing date) (Status) (published, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint

Ralph E. Bucknam, Reg. No. 14,814, Fernanda M. Fiordalisi, Reg. No. 20,938,
of BUCKNAM AND ARCHIER, Joseph J. Orlando, Reg. No. 25,218
600 Old Country Road, Garden City, New York 11530 -
Tel. No. (516) 222-8885

my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Wherefore I pray that Letters Patent be granted to me for the invention or discovery described and claimed in the foregoing specification and claims, and I hereby subscribe my name to the foregoing specification and claims, declaration, power of attorney, and this petition.

Full name of sole or first inventor Hiroshi HASEGAWA
Inventor's signature Hiroshi Hasegawa Date March 3, 1998
Residence c/o NIPPON OIL CO., LTD., CENTRAL TECHNICAL RESEARCH LABORATORY
Citizenship JAPAN 8, Chidori-cho, Naka-ku, Yokohama-shi, Kanagawa, JAPAN
Post Office Address Same as residence

Full name of second joint inventor, if any Noboru ISHIDA
Second inventor's signature Noboru Ishida Date March 3rd, 1998
Residence c/o NIPPON OIL CO., LTD., CENTRAL TECHNICAL RESEARCH LABORATORY
Citizenship JAPAN 8, Chidori-cho, Naka-ku, Yokohama-shi, Kanagawa, JAPAN
Post Office Address Same as residence

(Supply similar information and signature for third and subsequent joint inventors)

Declaration, Power of Attorney, and Petition

As a below named inventor, I hereby declare that:

Page 2 of 2

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled FLUID COMPOSITIONS CONTAINING REFRIGERATOR OILS AND CHLORINE-FREE FLUOROCARBON REFRIGERANTS

(check one) ☒ is attached hereto. ☐ was filed on _____ the specification of which
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Hei. 2-121133	Japan	May 15, 1990	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

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(Application Serial No.) (Filing date) (Status) (patented, pending, abandoned)
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint

Ralph E. Bucknam, Reg. No. 14,814, Fernanda M. Fiordalisi, Reg. No. 20,938,
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Wherefore I pray that Letters Patent be granted to me for the invention or discovery described and claimed in the foregoing specification and claims, and I hereby subscribe my name to the foregoing specification and claims, declaration, power of attorney, and this petition.

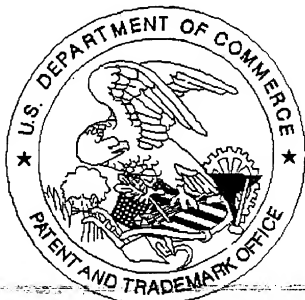
Full name of sole or first inventor Umekichi SASAKI
Inventor's signature Umekichi Sasaki Date March 3, 1998
Residence c/o NIPPON OIL CO., LTD., CENTRAL TECHNICAL RESEARCH LABORATORY
Citizenship JAPAN 8, Chidori-cho, Naka-ku, Yokohama-shi, Kanagawa, JAPAN
Post Office Address Same as residence

Full name of second joint inventor, if any Tatsuyuki ISHIKAWA
Second inventor's signature Tatsuyuki Ishikawa Date March 3, 1998
Residence c/o NIPPON OIL CO., LTD., CENTRAL TECHNICAL RESEARCH LABORATORY
Citizenship JAPAN 8, Chidori-cho, Naka-ku, Yokohama-shi, Kanagawa, JAPAN
Post Office Address Same as residence

(Supply similar information and signature for third and subsequent joint inventors)

United States Patent & Trademark Office

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